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D6

(54) Sheet or film of cyclo-olefin polymer

Folie oder Film aus einem Cycloolefinpolymer

Feuille ou film à base d'un polymère de cyclo-oléfine

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DD-A- 224 538

- WPIL, FILE SUPPLIER, AN=86-158638, Derwent Publications Ltd, London, GB;
- & JP-A-61 091 244 (NIPPON ZEON) 09-05-1986
- WPIL, FILE SUPPLIER, AN=90-088099, Derwent Publications Ltd, London, GB; & JP-A-2 042 441 (NIPPON ZEON) 13-02-1990

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description

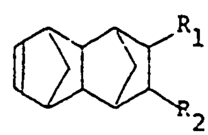
This invention relates to a sheet or a film formed of a cyclo-olefin polymer. More specifically, it relates to a sheet or a film having excellent elongation resistance, ease of tearing and gas-barrier property.

Polyethylene and polypropylene are shaped into a sheet or a film form and used frequently as packaging material for foods or as an adhesive tape. The food-packaging film and sheet are required to have excellent gas-barrier property and elongation resistance, and for ease of pack opening or the breaking of the adhesive tape, they are also required to have the property of being torn under a slight force (i.e. ease of tearing).

Conventional sheets or films formed of poly-ethylene and polypropylene are further required to have elongation resistance, gas-barrier property and ease of tear (easy openability).

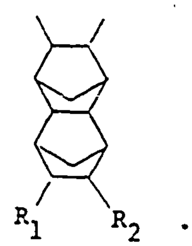
Japanese Laid-Open Patent Publication No. 26024/1985 discloses an optical material comprising as a constituent material a polymer obtained by hydrogenating a ring-opened polymer of 100 to 50 mole % of units of tetracyclododecene or its derivative and 0 to 50 mole % of units of norbornene or its derivative.

Japanese Laid-Open Patent Publication No. 168708/1985 discloses a random copolymer having an intrinsic viscosity, measured in decalin at 135 °C, of 0.5 to 10 dl/g and composed of ethylene and a compound represented by the following formula

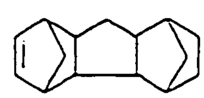


wherein R_1 and R_2 are identical or different and each represents a hydrogen atom, an alkyl group or a halogen atom.

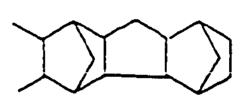
The mole ratio of ethylene to the above compound being from 10:90 to 90:10, the compound of the above formula mainly constituting structural units of the following formula



Japanese Laid-Open Patent Publication No. 223013/1988 discloses a polymer of a compound of the following formula

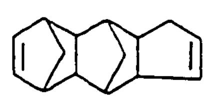


or a copolymer of the above compound and ethylene, the mole ratio of ethylene to the compound of the above formula being 95:5 to 0:100, and the compound of the above formula constituting structural units of the following formula.

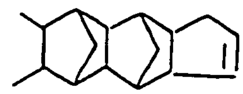


said polymer or copolymer having an intrinsic viscosity, measured in toluene at 25 °C, of 0.005 to 20 dl/g.

Japanese Laid-Open Patent Publication No. 243111/1988 is a polymer of a compound of the following formula

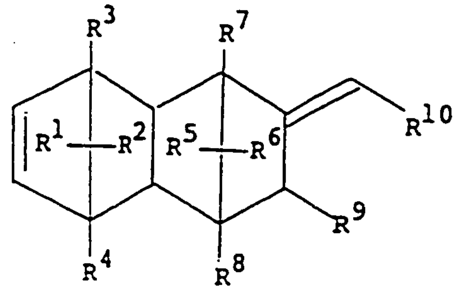


or a copolymer of the compound of the above formula with ethylene, the mole ratio of ethylene to the above compound being from 95:5 to 0:100, the compound of the above formula mainly constituting units of the following formula

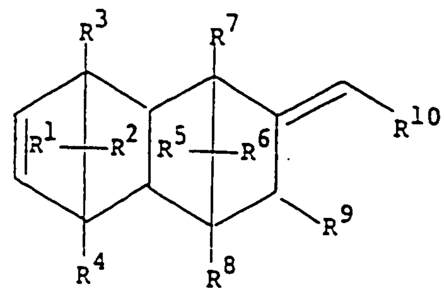


said polymer or copolymer having an intrinsic viscosity, measured in toluene at 25 °C, of 0.005 to 20 dl/g.

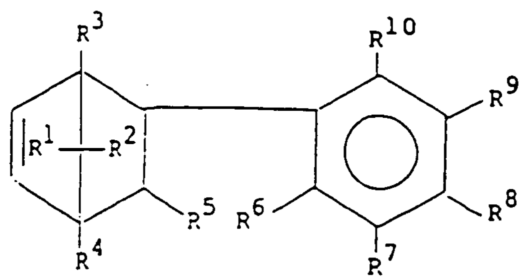
Japanese Laid-Open Patent Publication No. 305111/1988 discloses a random copolymer of ethylene with a compound of the following formula



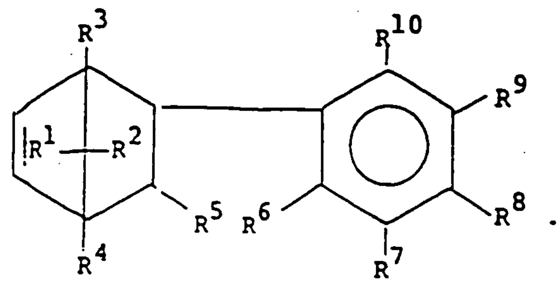
wherein R^1 to R^{10} are identical or different, and each represents a hydrogen atom or an alkyl group, and having an ethylene content of 50 to 90 mole % and an intrinsic viscosity, measured in decalin at 30 °C, of 0.3 to 10 dl/g, the compound of the above formula constituting units represented by the following formula.



Japanese Laid-Open Patent Publication No. 185307/1989 discloses a random copolymer composed of ethylene and a compound of the following formula



wherein R^1 to R^{10} are identical or different, and each represents a hydrogen atom or an alkyl group and R^5 may, together with R^6 or R^{10}, form an alkylene group having 1 to 3 carbon atoms,
and having an ethylene content of 50 to 90 mole % and an intrinsic viscosity, measured in decalin at 30 °C, of 0.3 to 10 dl/g, the compound of the above formula constituting units of the following formula

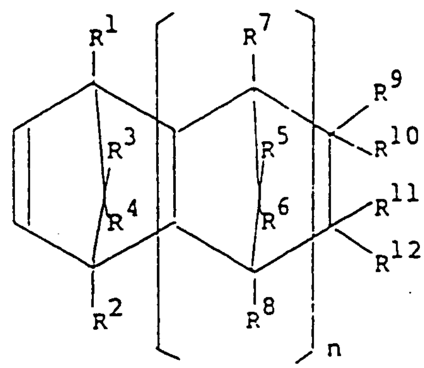


None of these patent documents describe sheets or films of these polymers or copolymers, and describe anything on gas-barrier property.

The present invention seeks to provide a sheet or a film having excellent elongation resistance, gas-barrier property and ease of tear.

The present invention thus provides a sheet or a film formed of an intimate mixture of:

(A) at least one cyclo-olefin polymer selected from ring-opened polymers derived from at least one cyclo-olefin of formula (I)



(I)

wherein n is 0 or a positive integer,
and each of R^1 to R^{12} independently represents hydrogen, a halogen or an aliphatic, aromatic or alicyclic hydrocarbon group;
or two of R^9 to R^{12} form, together with the carbon atoms to which they are bonded, a monocyclic or polycyclic group which may contain a double bond;
or R^9 and R^{10}, or R^{11} and R^{12} form an alkylidene group together with the carbon atoms to which they are bonded;

ring-opened copolymers derived from the cyclo-olefins of formula (I), hydrogenation products of said polymers or copolymers and addition polymers of the cyclo-olefins of formula (I) with ethylene, said cyclo-olefin polymer having an intrinsic viscosity [η], measured in decalin at 135°C, of 0.01 to 10 dl/g and a softening temperature of at least 70°C; and

(B) at least one crosslinked polymer selected from (1) a flexible copolymer comprising ethylene, another alpha-olefin, and a cyclo-olefin of formula (I), which cyclo-olefin may be the same or different from the cycloolefin used in component (A) and which has an intrinsic viscosity, measured in decalin at 135°C, of 0.01 to 10 dl/g, and a glass transition temperature of not more than 0°C, (2) amorphous or low-crystalline alpha-olefin copolymers formed from at least two alpha-olefins and having a glass transition temperature of not more than 0°C, (3) alpha-olefin/diene copolymers formed from at least two alpha-olefins and at least one conjugated diene and having a glass transition temperature of not more than 0°C, (4) aromatic vinyl hydrocarbon/conjugated diene random or block copolymers or hydrogenation products thereof having a glass transition temperature of not more than 0°C, and (5) flexible copolymers formed from isobutylene and flexible copolymers formed from isobutylene and conjugated dienes.

The above sheet or film has excellent elongation resistance, gas-barrier property and ease of tear.
The above sheets or films have excellent gas-barrier properties characterized by having lower permeability of

gases such as oxygen and carbon dioxide gas than conventional films.

Accordingly, by using the sheet or film of this invention as a packaging material, foods, for example, can be stored for a longer period of time.

Futhermore the sheet or film of the invention has excellent elongation resistance. Specifically, since the sheet or film of this invention has a high elasticity modulus and a low elongation at break, when it is stretched it is elongated or deformed only to a limited extent unlike conventional films, and is thus suitable for packaging applications.

Furthermore, the sheet or film of this invention has excellent ease of tearing, and when used as a packaging material, the package can be easily opened.

The sheet or film obtained from the cyclo-olefin polymer in accordance with this invention will now be further described.

cyclo-Olefins

The cyclo-olefin polymer constituting the sheet or film of the invention is selected from ring-opened polymers derived from the cyclo-olefins of formula (I), ring-opened copolymers derived from the cyclo-olefins of formula (I), hydrogenation products of said polymers or copolymers, and addition polymers of the cyclo-olefins of formula (I) with ethylene.

These cyclo-olefin polymers may be used singly or in combination.

In formula (I), R^1 to R^{12}, independently from each other, represent a hydrogen atom, a halogen atom or a hydrocarbon group. The halogen atom may be, for example, fluorine, chlorine, bromine or iodine.

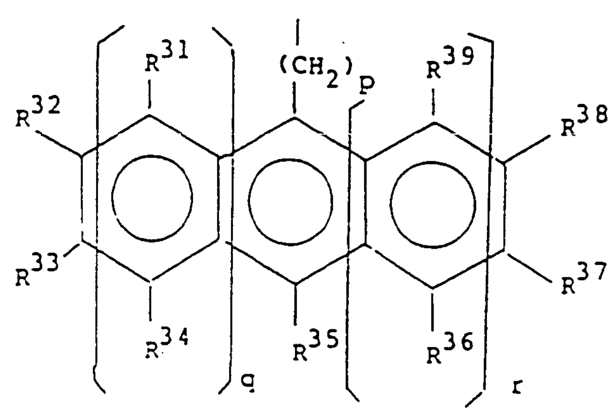
The hydrocarbon groups may include alkyl groups, alkenyl groups, cycloalkyl groups, aryl groups, aralkyl groups, and alkylaryl groups.

The alkyl groups may be linear or branched, and preferably have 1 to 20 carbon atoms.

The alkenyl groups have at least one carbon-carbon double bond, and preferably contain 2 to 20 carbon atoms.

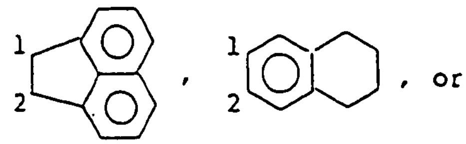
The cycloalkyl groups preferably have 3 to 15 carbon atoms.

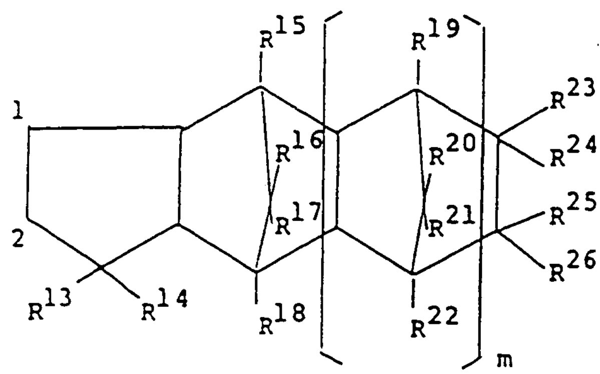
The aryl groups preferably have 6 to 14 carbon atoms. The aralkyl and alkylaryl groups are preferably composed of an alkyl group having 1 to 6 carbon atoms further attached to the above aryl group. Examples of preferred aryl and alkylaryl groups are groups of formula



wherein p is 0 or an integer of at least 1, preferably 0, 1 or 2; q and r are 0, 1 or 2; and each of R^{31} to R^{39} independently represents hydrogen, a halogen, an alkoxy group, an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

Two of R^9 and R^{12}, particularly adjoining R^9 and R^{10}, or R^{11} and R^{12} may, together with the carbon atoms to which they are bonded, form a monocyclic or polycyclic group which may contain a double bond. Examples of the monocyclic or polycyclic group are

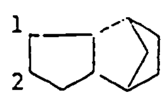




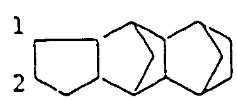
wherein R^{13} to R^{26} independently represents hydrogen a halogen atom and or an aliphatic, aromatic or alicyclic hydrocarbon group; or two of R^{23} to R^{26} form, together with the carbon atoms to which they are bonded, a monocyclic or polycyclic group which may include a double bond; or R^{23} and R^{24}, or R^{25} and R^{26}, form, together with the carbon atoms to which they are bonded, an alkylidene group; an m is 0 or a positive integer.

It should be understood that each of the carbon atoms marked 1 and 2 is the carbon atoms to which R^9 and R^{10} are bonded or R^{11} and R^{12} are bonded.

Examples of the groups of the above formula having R^{13} to R^{26} groups are those in which all of R^{13} to R^{26} are hydrogen atoms, such as

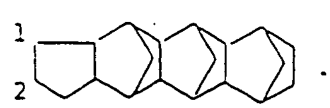


(m=0)



(m=1)

and

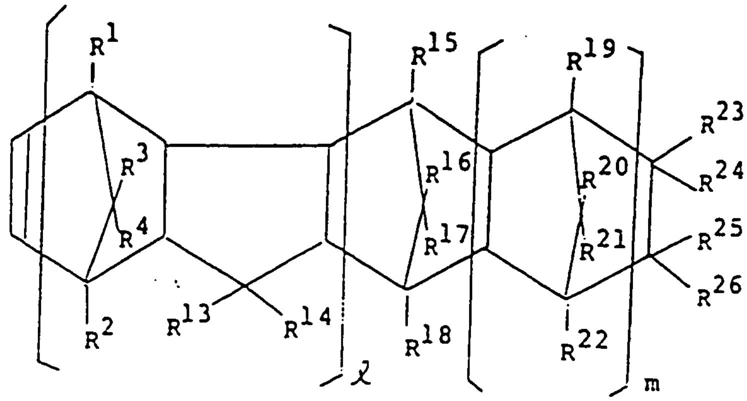


(m=2)

The monocyclic and polycyclic groups other than the groups represented by the above formula having R^{13} to R^{26} groups may be substituted by an alkyl group such as methyl.

In formula (I), R^9 and R^{10}, or R^{11} and R^{12} may each form an alkylidene group together with the carbon atoms to which they are bonded. The alkylidene groups formed by R^9 to R^{12} may be substituted by a substituent such as an ester group.

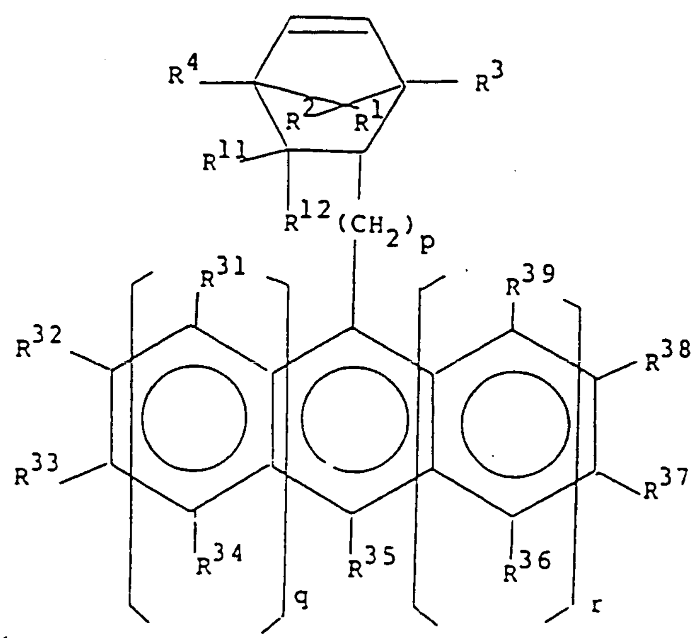
cyclo-olefins of formula (II)



(II)

wherein R^1 to R^4, R^{13} to R^{26} and m are as defined above, and ℓ is 0 or 1, are preferred. Formula (II) corresponds to formula (I) in which n is 0, and R^9 and R^{10}, or R^{11} and R^{12} are bonded to each other to form a monocyclic or polycyclic group.

A group of cyclo-olefins of formula (II-a)



(II-a)

wherein R^1 to R^4, R^{11}, R^{12}, R^{31} to R^{39}, p, q and r are as defined above or R^{11} or R^{12} and R^{31} or R^{32} may together form a direct bond or an alkylene group having 1 to 3 carbon atoms, also constitute compounds of formula (I).

Formula (II-a) corresponds to formula (I) in which n is 0 and R^9 or R^{10} correspond to groups exemplified above as the aryl group of the alkylaryl group.

Examples of the cyclo-olefins of formula (I) include

bicyclo[2.2.1]hept-2-ene derivatives,
tetracyclo[4.4.0.$1^{2.5}$.$1^{7.10}$]-3-dodecene derivatives,
hexacyclo[6.6.1.$1^{3.6}$.$1^{10.13}$.$0^{2.7}$.$0^{9.14}$]-4heptadecene derivatives,
octacyclo[8.8.0.$1^{2.9}$.$1^{4.7}$.$1^{11.18}$.$1^{13.16}$.$0^{3.8}$.$0^{12.17}$]-5-docosene derivatives,
pentacyclo[6.6.1.$1^{3.6}$.$0^{2.7}$.$0^{9.14}$]-4-hexadecene derivatives,
heptacyclo-5-eicosene derivatives,
heptacyclo-5-heneicosene derivatives,
tricyclo[4.3.0.$1^{2.5}$]-3-decene derivatives,
tricyclo[4.3.0.$1^{2.5}$]-3-undecene derivatives,

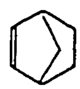
pentacyclo[6,5,1,$1^{3.6}$,$0^{2.7}$,$0^{9.13}$]-4-penta-decene derivatives,
pentacyclopentadecadiene derivatives,
pentacyclo[4,7,0,$1^{2.5}$,$0^{8.13}$,$1^{9.12}$]-3-penta-decene derivatives,
heptacyclo[7,8,0,$1^{3.6}$,$0^{2.7}$,$1^{10.17}$,$0^{11.16}$,$1^{12.15}$]-4-eicosene derivatives, and
nonacyclo[9,10,1,$1^{4.7}$,$0^{3.8}$,$0^{2.10}$,$0^{12.21}$,$1^{13.20}$,$0^{14.19}$,$1^{15.18}$]-5-pentacosene derivatives.

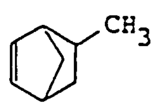
Thus, in compounds of formula (I), each of R^1 to R^{12} may, independently, represent a linear or branched C_1-C_{20} alkyl group, a cyclohexyl group or an optionally substituted phenyl group; or either R^9 or R^{10}, together with either R^{11} or R^{12} form, with the carbon atoms to which they are attached, a monocyclic or polycyclic hydrocarbon group, optionally substituted by a C_1-C_6 alkyl group and containing from 5 to 20 carbon atoms in the cyclic system.

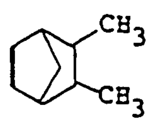
Typically the linear or branched C_1-C_{20} alkyl group is a C_1-C_{15}, preferably a C_1-C_{10}, more preferably a C_1-C_6 alkyl group.

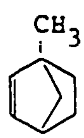
Specific Examples of cyclo-olefins of formula (I) are given below.

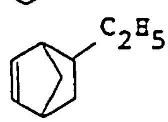
(1) bicyclo[2.2.1]hept-2-ene derivatives such as

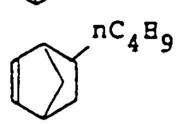

bicyclo[2,2,1]hept-2-ene

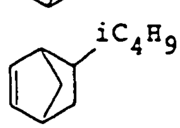

6-methylbicyclo[2,2,1]-hept-2-ene

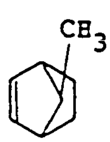

5,6-dimethylbicyclo-[2,2,1]hept-2-ene


1-methylbicyclo-[2,2,1]hept-2-ene

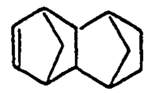

6-ethylbicyclo-[2,2,1]hept-2-ene


6-n-butylbicyclo-[2,2,1]hept-2-ene

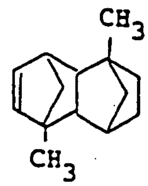

6-isobutylbicyclo-[2,2,1]hept-2-ene


7-methylbicyclo[2,2,1]-hept-2-ene

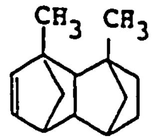
(2) tetracyclo[4.4.0.$1^{2.5}$.$1^{7.10}$]-3-dodecene derivatives such as



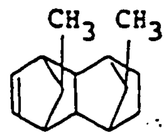
tetracyclo[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



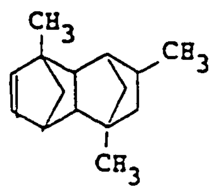
5,10-dimethyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



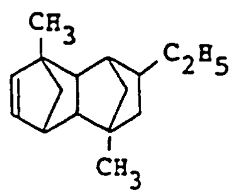
2,10-dimethyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecane



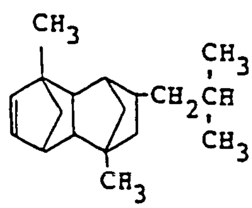
11,12-dimethyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecane



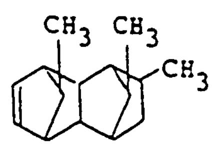
2,7,9-trimethyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



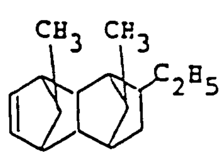
9-ethyl-2,7-dimethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



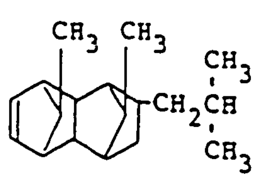
9-isobutyl-2,7-dimethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



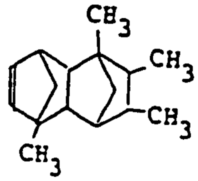
9,11,12-trimethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



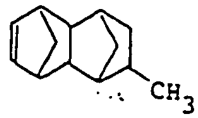
9-ethyl-11,12-dimethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



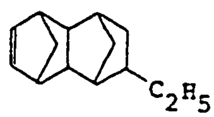
9-isobutyl-11,12-dimethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



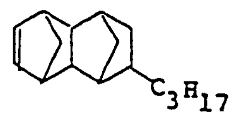
5,8,9,10-tetramethyltetracyclo[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



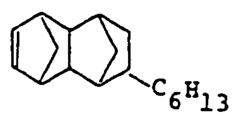
8-methyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



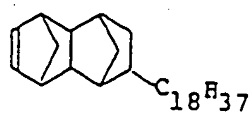
8-ethyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



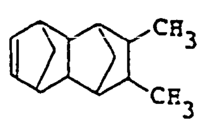
8-propyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



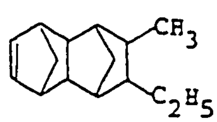
8-hexyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



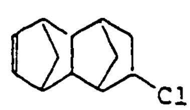
8-stearyltetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



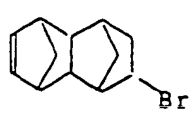
8,9-dimethyltetracyclo[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



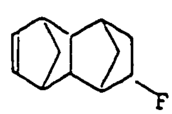
8-methyl-9-ethyltetracyclo[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



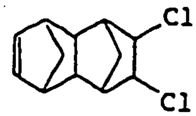
8-chlorotetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



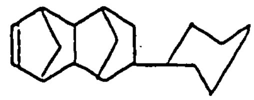
8-bromotetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



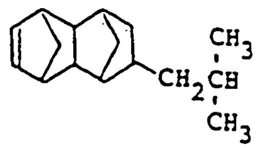
8-fluorotetracyclo-[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene



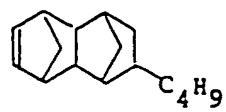
8,9-dichlorotetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



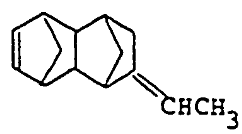
8-cyclohexyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



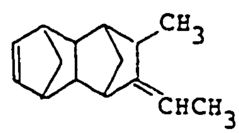
8-isobutyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



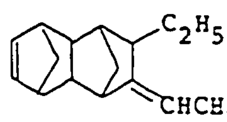
8-butyltetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



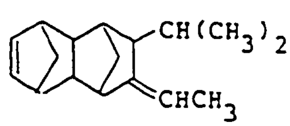
8-ethylidenetetracyclo-$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



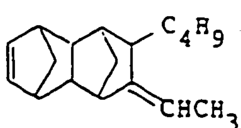
8-ethylidene-9-methyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



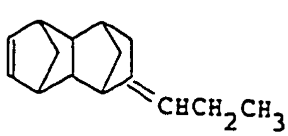
8-ethylidene-9-ethyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



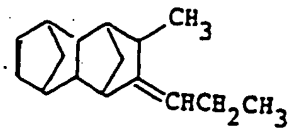
8-ethylidene-9-isopropyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



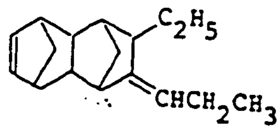
8-ethylidene-9-butyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



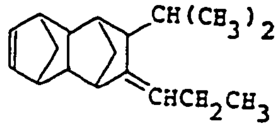
8-n-propylidenetetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



8-n-propylidene-9-methyl-tetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene

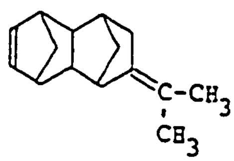


8-n-propylidene-9-ethyl-tetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene

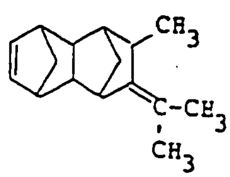


8-n-propylidene-9-iso-propyltetacyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene

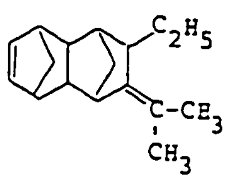
8-n-propylidene-9-butyl-tetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



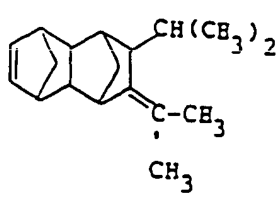
8-isopropylidene-tetra-cyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



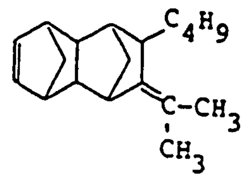
8-isopropylidene-9-methyl-tetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene



8-isopropylidene-9-ethyl-tetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene

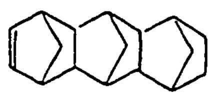


8-isopropylidene-9-iso-propyltetracyclo$[4,4,0,1^{2,5},1^{7,10}]$-3-dodecene

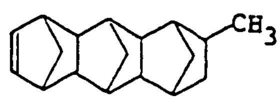


8-isopropylidene-9-butyl-tetracyclo[4,4,0,$1^{2,5}$,$1^{7,10}$]-3-dodecene

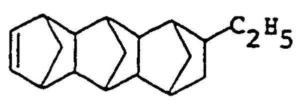
(3) hexacyclo[6.6.1.$1^{3.6}$.$1^{10.13}$.$0^{2.7}$.$0^{9.14}$]-4-heptadecene derivatives such as



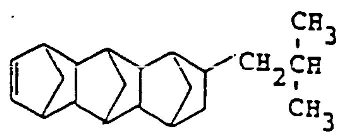
hexacyclo[6,6,1,$1^{3,6}$,$1^{10,13}$,$0^{2,7}$,$0^{9,14}$]-4-heptadecene



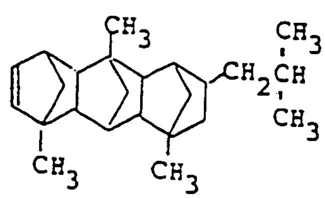
12-methylhexacyclo[6,6,1,$1^{3,6}$,$1^{10,13}$,$0^{2,7}$,$0^{9,14}$]-4-heptadecene



12-ethylhexacyclo[6,6,1,$1^{3,6}$,$1^{10,13}$,$0^{2,7}$,$0^{9,14}$]-4-heptadecene

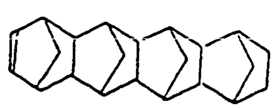


12-isobutylhexacyclo[6,6,1,$1^{3,6}$,$1^{10,13}$,$0^{2,7}$,$0^{9,14}$]-4-heptadecene

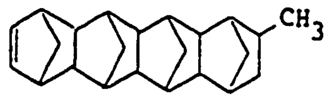


1,6,10-trimethyl-12-isobutylhexacyclo[6,6,1,$1^{3,6}$,$1^{10,13}$,$0^{2,7}$,$0^{9,14}$]-4-heptadecene

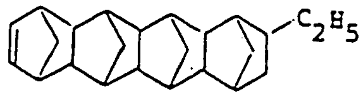
(4) octacyclo[8.8.0.$1^{2.9}$.$1^{4.7}$.$1^{11.18}$.$1^{13.16}$.$0^{3.8}$.$0^{12.17}$]-5-docosene derivatives such as



octacyclo[8,8,0,$1^{2,9}$,$1^{4,7}$,$1^{11,18}$,$1^{13,16}$,$0^{3,8}$,$0^{12,17}$]-5-docosene

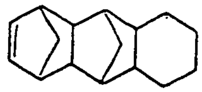


15-methyloctacyclo[8,8,0,$1^{2,9}$,$1^{4,7}$,$1^{11,18}$,$1^{13,16}$,$0^{3,8}0^{12,17}$]-5-docosene

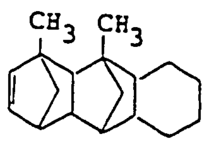


15-ethtyloctacyclo[8,8,0,$1^{2,9}$,$1^{4,7}$,$1^{11,18}$,$1^{13,16}$,$0^{3,8}$,$0^{12,17}$]-5-docosene

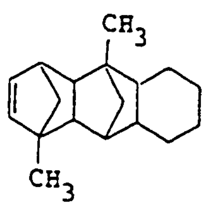
(5) <u>pentacyclo[6.6.1.$1^{3.6}$.$0^{2.7}$.$0^{9.14}$]-4-hexadecene derivatives</u> such as



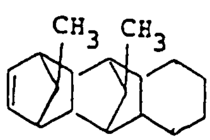
pentacyclo[6,6,1,$1^{3,6}$,$0^{2,7}$,$0^{9,14}$]-4-hexadecene



1,3-dimethylpentacyclo-[6,6,1,$1^{3,6}$,$0^{2,7}$,$0^{9,14}$]-4-hexadecene

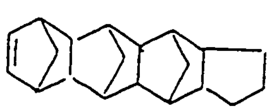


1,6-dimethylpentacyclo-[6,6,1,$1^{3,6}$,$0^{2,7}$,$0^{9,14}$]-4-hexadecene

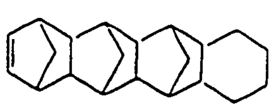


15,16-dimethylpentacyclo-[6,6,1,$1^{3,6}$,$0^{2,7}$,$0^{9,14}$]-4-hexadecene

(6) <u>heptacyclo-5-icosene or heptacyclo-5-heneicosene derivatives</u> such as

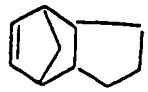


heptacyclo[8,7,0,$1^{2,9}$,$1^{4,7}$,$1^{11,17}$,$0^{3,8}$,$0^{12,16}$]-5-icosene

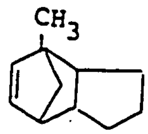


heptacyclo[8,7,0,$1^{2,9}$,$1^{4,7}$,$1^{11,18}$,$0^{3,8}$,$0^{12,17}$]-5-heneicosene

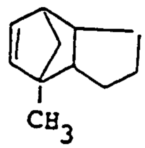
(7) tricyclo[4.3.0.1^{2.5}]-3-decene derivatives such as



tricyclo[4,3,0,$1^{2,5}$]-3-decene

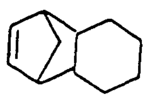


2-methyltricyclo[4,3,0,$1^{2,5}$]-3-decene

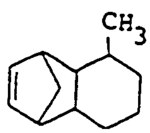


5-methyltricyclo[4,3,0,$1^{2,5}$]-3-decene

(8) tricyclo[4.4.0.$1^{2.5}$]-3-undecene derivatives such as

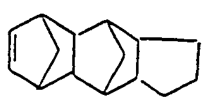


tricyclo[4,4,0,$1^{2,5}$]-3-undecene

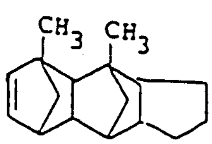


10-methyltricyclo[4,4,0,$1^{2,5}$]-3-undecene

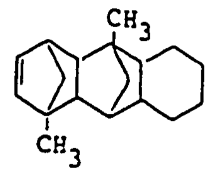
(9) pentacyclo[6.5.1.$1^{3.6}$.$0^{2.7}$.$0^{9.13}$]-4-pentadecene derivatives such as



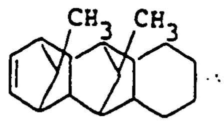
pentacyclo[6,5,1,$1^{3,6}$,$0^{2,7}$,$0^{9,13}$]-4-pentadecene



1,3-dimethylpentacyclo[6,5,1,$1^{3,6}$,$0^{2,7}$,$0^{9,13}$]-4-pentadecene

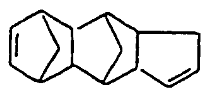


1,6-dimethylpentacyclo[6,5,1,$1^{3,6}$,$0^{2,7}$,$0^{9,13}$]-4-pentadecene



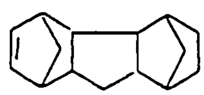
14,15-dimethylpentacyclo[6,5,1,$1^{3,6}$,$0^{2,7}$,$0^{9,13}$]-4-pentadecene

(10) diene compounds such as

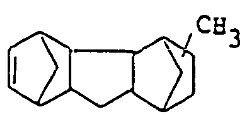


pentacyclo[6,5,1,$1^{3,6}$,$0^{2,7}$,$0^{9,13}$]-4,10-pentadecadiene

(11) pentacyclo[4.7.0.$1^{2.5}$.$0^{8.13}$.$1^{9.12}$]-3-pentadecene derivatives such as

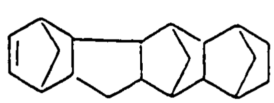


pentacyclo[4,7,0,$1^{2,5}$,$0^{8,13}$,$1^{9,12}$]-3-pentadecene

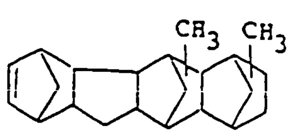


methyl-substituted pentacyclo[4,7,0,$1^{2,5}$,$0^{8,13}$,$1^{9,12}$]-3-pentadecene

(12) heptacyclo[7.8.0.$1^{3.6}$.$0^{2.7}$.$1^{10.17}$.$0^{11.16}$.$1^{12.15}$]-4-eicosene derivatives such as

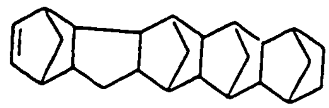


heptacyclo[7,8,0,$1^{3,6}$,$0^{2,7}$,$1^{10,17}$,$0^{11,16}$,$1^{12,15}$]-4-eicosene

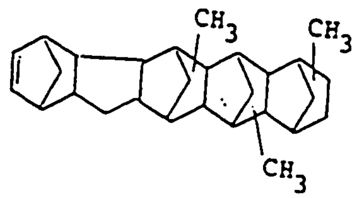


dimethyl-substituted heptacyclo[7,8,0,$1^{3,6}$,$0^{2,7}$,$1^{10,17}$,$0^{11,16}$,$1^{12,15}$]-4-eicosene

(13) <u>nonacyclo[9.10.1.1$^{4.7}$.0$^{3.8}$.0$^{2.18}$.0$^{12.21}$.1$^{13.20}$.0$^{14.19}$.1$^{15.18}$]-5-pentacosene derivatives</u> such as

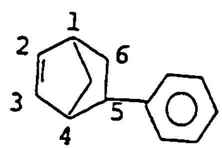


nonacyclo[9,10,1,1^{4,7},0^{3,8},0^{2,18},0^{12,21},1^{13,20},0^{14,19},1^{15,18}]-5-pentacosene

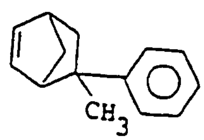


trimethyl substituted nonacyclo[9,10,1,1^{4,7},0^{3,8},0^{2,18},0^{12,21},1^{13,20},0^{14,19},1^{15,18}]-5-pentacosene.

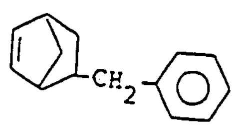
Other examples include:



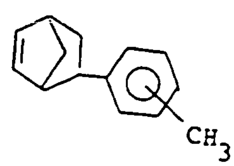
5-phenyl-bicyclo[2,2,1]hept-2-ene



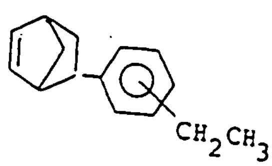
5-methyl-5-phenyl-bicyclo-[2,2,1]hept-2-ene



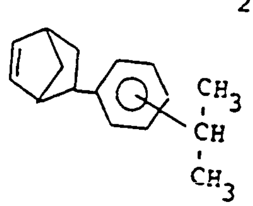
5-benzyl-bicyclo[2,2,1]hept-2-ene



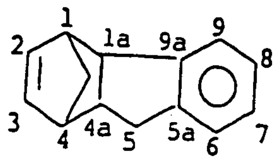
5-tolyl-bicyclo[2,2,1]hept-2-ene



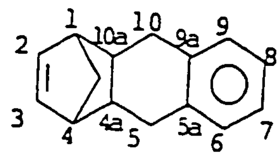
5-(ethylphenyl)-bicyclo-[2,2,1]hept-2-ene



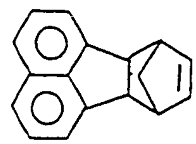
5-(isopropylphenyl)-bicyclo[2,2,1]hept-2-ene



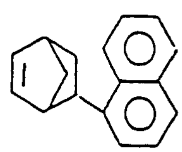
1,4-methano-1,1a,4,4a-tetra-hydrofluolene



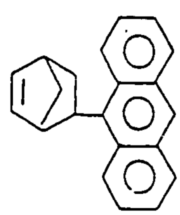
1,4-methano-1,4,4a,5,10,10a-hexahydroanthracene



cyclopentadiene-acenaphthyl-ene adduct



5-(α-naphthyl)-bicyclo-[2,2,1]-hept-2-ene, and



5-(anthracenyl)-bicyclo-[2,2,1]-hept-2-ene.

In addition to the above examples, further examples of the polycyclic olefins of formula (I) include octahydronaphthalenes such as 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene. 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-n-butyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and 2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.

These cyclo-olefins may be used singly or in combination.

The cyclo-olefins of formula (I) or preferably formula (II) may be easily produced by condensing cyclo-pentadienes with the corresponding olefins or cyclo-olefins by the Diels-Alder reaction.

Cyclo-Olefin Polymer

The cyclo-olefin polymer constituting the sheet or film in this invention is at least one type of polymer selected from

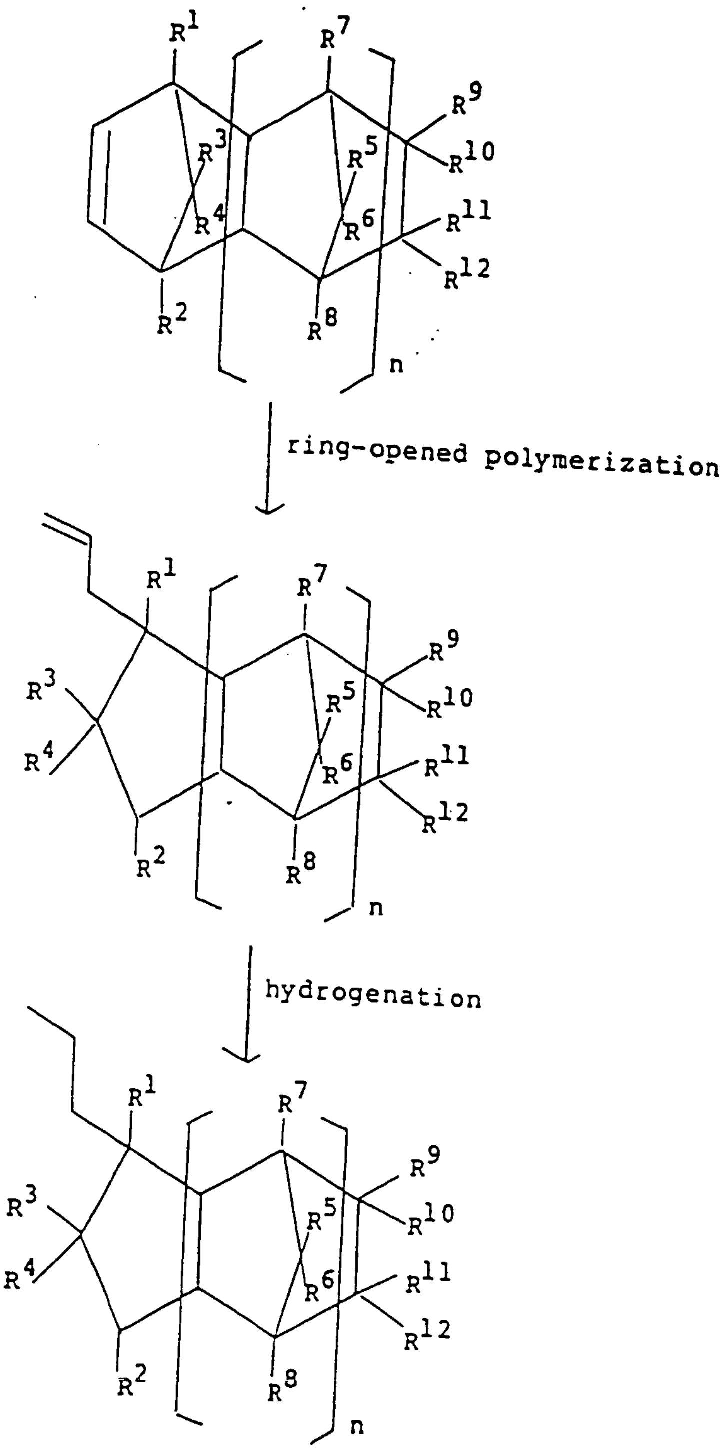
(1-a) ring-opened polymers or copolymers derived from the cyclo-olefins of formula (I),
(1-b) hydrogenation products of these polymer or copolymers, and
(2) addition polymers of ethylene with the cyclo-olefins of formula (I).

The ring-opened polymers or copolymers (1-a) derived from the cyclo-olefins of formula (I) and the hydrogenation products of these polymers or copolymers (1-b) will first be described.

The ring-opened polymers of the cyclo-olefins may be prepared by ring-opening polymerization of the cyclo-olefins of formula (I) [including formulae (II) and (II-a)] by methods known per se. Typical examples of such ring-opened polymers or copolymers include (co)polymers of 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalenes with each other, and ring-opned copolymers of 1,3,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalenes with norbornene (bicyclo[2.3.1]hept-2-ene).

Double bonds remain in the cyclo-olefin ring-opened polymers prepared as above. They may be easily hydrogenated by known methods. In the present invention, hydrogenation products of the cyclo-olefins ring-opened (co)polymers may also be used. Hydrogenation further improves thermal stability and weather resistance.

The ring-opened (co)polymers and hydrogenation products of these are believed to assume the following structure.



In the ring-opening polymerization, cyclo-olefins other than the cyclo-olefins of formula (I) [including formulae (II) and (II-a)] may be copolymerized. Examples of the other cyclo-olefins include cyclobutene, cyclopentene, cyclohexene, 3,4-dimethyl-cyclopentene, 3-methylcyclohexene, 2-(2-methylbutyl)-1-cyclohexene, 2,3,3a,7a-tetrahydro-4,7-methano-1H-indene and 3a,5,6,7a-tetrahydro-4,7-methano-1H-indene so long as it does not impair the properties of the cyclo-olefin ring-opened (co)polymers and their hydrogenation products.

The other cyclo-olefin may usually be employed in a proportion of not more than 20 mole %.

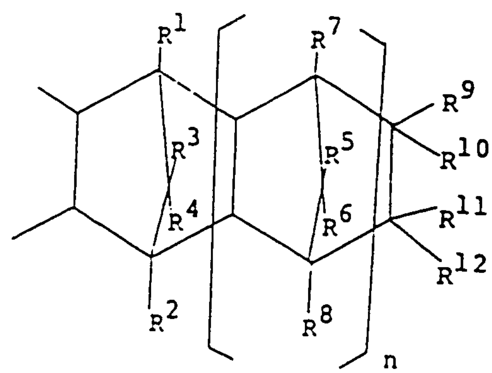
The addition polymers of ethylene with cyclo-olefins are the addition polymers of ethylene with the cyclo-olefins of formula (I) including formula (II) and (II-a).

In the addition polymers, ethylene is used in a proportion of preferably 40 to 85 mole %, especially preferably 50 to 75 mole %, and the cyclo-olefin is used in a proportion of preferably 15 to 60 mole %, especially preferably 25 to 50 mole %. Specifically, in the cycloolefin/ethylene addition polymers, the recurring units derived from ethylene and the recurring units derived from cyclo-olefin are bonded in a mole ratio of preferably from 40:60 to 85:15, especially preferably from 50:50 to 75:25.

The cyclo-olefin/ethylene addition polymers can be produced by polymerizing ethylene and the cyclo-olefin in the presence of a catalyst formed from a hydrocarbon-soluble vanadium compound and a halogen-containing organoaluminium compound in a hydrocarbon medium.

Such a polymerization method is already known, and is proposed, for example, in Japanese Laid-Open Patent Publication No. 168708/1985.

It is believed that in the cyclo-olefin/ ethylene addition polymers, at least part of the cyclo-olefin of formula (I) is randomly bonded to the recurring units derived from ethylene in the form of recurring units of formula (I').



(I')

wherein R^1 to R^{12} and n are as defined above.

In the present invention, the cyclo-olefin/ethylene addition polymer may also be an addition polymer of ethylene and the cyclo-olefin of formula (I) with an alpha-olefin other than ethylene and a cyclo-olefin other than the cyclo-olefin of formula (I) copolymerized therewith such that the properties of the copolymer are not impaired.

The other alpha-olefin is linear or branched. Examples of the alpha-olefin are alpha-olefins having 3 to 20 carbon atoms, such as propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferably, alpha-olefins having 3 to 15 carbon atoms, especially 3 to 10 carbon atoms, are used.

The cyclo-olefin other than the cyclo-olefins of formula (I) includes, for example, cyclobutene, cyclopentene, cyclohexene, 3,4-dimethylcyclopentene, 3-methylcyclohexene, 2-(2-methylbutyl)-1-cyclohexene, alpha-methylstyrene, 2,3,3a,7a-tetrahydro-4,7-methano-1H-indene and 3a,5,6,7a-tetrahydro-4-methano-1H-indene.

When the other alpha-olefin and the other cyclo-olefin have two or more double bonds in the molecule, double bonds remaining unused in the addition polymerization may be hydrogenated to improve weatherability.

By the above addition and hydrogenation, the cyclo-olefin/ethylene addition polymer used in this invention usually has an iodine value of not more than 5, generally not more than 1.

It can be determined by ^{13}C-NMR measurement that the cyclo-olefin of formula (I) used as a starting material has a structure of the above formula (I') in the cyclo-olefin/ethylene addition polymer. The cycloolefin/ethylene addition polymer has a chemically stable structure and excellent heat aging resistance.

The cyclo-olefin ring-opened (co)polymers (1-a), the hydrogenation products (I-b) and the cycloolefin/ethylene addition polymers (2) have an intrinsic viscosity, measured in decalin at 135 °C, of usually 0.01 to 20 dl/g, preferably 0.01 to 10 dl/g, especially 0.05 to 8 dl/g, further preferably 0.05 to 5 dl/g, most preferably 0.05 to 5 dl/g.

These cyclo-olefin polymers are generally amorphous or low-crystalline, preferably amorphous, and therefore have good transparency. Specifically, these cyclo-olefin polymers have a crystallinity, determined by X-ray diffractometry, of preferably 0 to 10 %, more preferably 0 to 7 %, especially preferably 0 to 5 %, and mostly 0 %. When these cyclo-olefin polymers are measured by a differential scanning calorimeter (DSC), melting points mostly are not observed.

These cyclo-olefin polymers are also characterized by having a high glass transition temperature (Tg) and a high softening temperature (TMA). They have a glass transition temperature of usually 50 to 230 °C, generally 70 to 210 °C, and a softening temperature of usually at least 70 °C, preferably 70 to 250 °C, especially 90 to 250 °C, further

preferably 90 to 230 °C, most preferably 100 to 200 °C. The cyclo-olefin polymers also generally have a heat decomposition temperature of 350 to 420 °C, mostly 370 to 400 °C.

As mechanical properties, they have a flexural modulus of usually 1×10^4 to 5×10^4 kg/cm², and a flexural strength of usually 300 to 1500 kg/cm².

They generally have a density of 0.86 to 1.10 g/cm², mostly 0.88 to 1.08 g/cm², and a refractive index, measured in accordance with ASTM-D542, of generally 1.47 to 1.58, mostly 1.48 to 1.56. Furtheremore, since the cyclo-olefin polymers are substantially amorphous, they have a haze (ASTM-D1003) of usually not more than 20 %, generally not more than 10 %.

As electrical properties, they generally have a dielectric constant (1 KHz), measured in accordance with ASTM-D150, of 1.5 to 3.0, preferably 1.9 to 2.6, and generally have a dielectric loss tangent of 9×10^{-4} to 8×10^{-5}, preferably 3×10^{-4} to 9×10^{-5}.

The film or sheet of the invention is formed from an intimate mixture of the cyclo-olefin polymer and another polymer, for example a polymer alloy. The other polymers will be described below.

They are rubber components in which a crosslinked structure is formed selected from (1) to (5):

(1) flexible copolymers of ethylene, another alpha-olefin, and the cyclo-olefin of formula (I), which have a intrinsic viscosity, measured in decalin at 135 °C, of 0.01 to 10 dl/g, and a glass transition temperature of not more than 0 °C,
(2) amorphous or low-crystalline alpha-olefin copolymers formed from at least two alpha-olefins and having a glass transition temperature of not more than 0 °C,
(3) alpha-olefin/diene copolymers formed from at least two alpha-olefins and at least one conjugated diene and having a glass transition temperature of not more than 0 °C,
(4) aromatic vinyl hydrocarbon/conjugated diene random or block copolymers or hydrogenation products thereof having a glass transition temperature of not more than 0 °C, and
(5) flexible polymers formed from isobutylene and flexible copolymers formed from isobutylene and conjugated dienes.

(1) Flexible polymers containing units derived from cyclo-olefins

The flexible polymers containing units derived from cyclo-olefins can be prepared by copolymerizing ethylene, the cyclo-olefin of formula (I), for example one of formula (II) or (II-a) described above, and an alpha-olefin. The olefins are preferably alpha-olefins having 3 to 20 carbon atoms. Examples of preferred alpha-olefins for use in this invention include propylene, 1-butene, 4-methyl-1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

Cyclo-olefins or cyclodienes such as ethylidene norbornene and dicyclopentadiene may used besides the above alpha-olefins or together with the alpha-olefins.

In the flexible polymers (1) containing units derived from cyclo-olefins, the recurring units derived from ethylene are generally contained in a proportion of 40 to 98 mole %, preferably 50 to 90 mole %, and the recurring units derived from the alpha-olefin are generally contained in a proportion of 2 to 50 mole %. The recurring units derived from cyclo-olefin are generally contained in a proportion of 2 to 20 mole %, preferably 2 to 15 mole %.

Unlike the above cyclo-olefin polymers, the flexible polymers (1) have a glass transition temperature of not more than 0 °C, preferably not more than -10 °C, and an intrinsic viscosity, measured in decalin at 135 °C, of 0.01 to 10 dl/g, preferably 0.08 to 7 dl/g. The flexible polymers (I) generally have a crystallinity, measured by X-ray diffractometry, of 0 to 10 %, preferably 0 to 7 %, especially preferably 0 to 5 %.

The flexible polymers (1) may be produced under properly selected conditions in the methods described, for example, in Japanese Laid-Open Patent Publications Nos. 168708/1985, 120816/1985, 115912/1985, 115916/1985, 271308/1986, 272216/1986, and 252406/1987.

(2) Alpha-olefin copolymers

The alpha-olefin copolymers (2) used as the flexible polymers are amorphous or low-crystalline copolymers of at least two types of alpha-olefins. Examples of low-crystalline copolymers are ethylene/alpha-olefin copolymers and propylene/alpha-olefin copolymers.

As the alpha-olefins constituting the ethylene/alpha-olefin copolymers, alpha-olefins having 3 to 20 carbon atoms are usually suitable. Specific examples are propylene, 1-butene, 4-methyl-1-butene, 1-hexene, 1-octene, 1-decene and mixtures of these. Among them, alpha-olefins having 3 to 10 carbon atoms are especially preferred.

In the ethylene/alpha-olefin copolymers, the mole ratio of the recurring units derived from ethylene to the recurring units derived from alpha-olefin is preferably adjusted to from 40:60 to 95:5, although it varies depending upon the type of the alpha-olefin. The above mole ratio is preferably from 40:60 to 90:10 if the alpha-olefin used is propylene. If the

alpha-olefin has 4 or more carbon atoms, the above mole ratio is preferably from 50:50 to 95:5.

As the alpha-olefins constituting the propylene/alpha-olefin copolymers, alpha-olefins having 4 to 20 carbon atoms are generally used. Specific examples are 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene and mixtures of these. Alpha-olefins having 4 to 10 carbon atoms are especially preferred.

In the above propylene/alpha-olefin copolymers, the mole ratio of the recurring units derived from propylene to the recurring units derived from the alpha-olefins is preferably from 50:50 to 95:5 although it may vary depending upon the type of the alpha-olefin.

(3) Alpha-olefin/diene copolymers

Ethylene/alpha-olefin/diene copolymer rubbers and propylene/alpha-olefin/diene copolymer rubbers are used as the alpha-olefin diene copolymers (3) used as the flexible polymers.

Alpha-olefins constituting such copolymer rubbers usually have 3 to 20 carbon atoms (4 to 20 carbon atoms in the case of the propylene/alpha-olefin). Examples include propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene and mixtures of these. Of these, alpha-olefins having 3 to 10 carbon atoms are especially preferred.

Examples of the dienes constituting these copolymer rubbers include aliphatic non-conjugated dienes such as 1,4-hexadiene, 1,6-octadiene, 2-methyl-1,5-hexadiene, 6-methyl-1,5-heptadiene and 7-methyl-1,6-octadiene; cyclic non-conjugated dienes such as cyclohexadiene, dicyclopentadiene, methyltetrahydroindene, 5-vinylnorbornene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-isopropylidene-2-norbornene and 6-chloromethyl-5-isopropenyl-2-norbornene; and 2,3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene and 2-propenyl-2,2-norbornadiene.

In the ethylene/alpha-olefin/diene copolymer rubbers, the mole ratio of the recurring units derived from ethylene to the recurring units derived from alpha-olefin is preferably from 40:60 to 90:10 in general, although it may vary depending upon the type of the alpha-olefin.

The content of the recurring units derived from the diene in these copolymer rubbers is usually 1 to 20 mole %, preferably 2 to 15 mole %.

(4) Aromatic vinyl hydrocarbon-conjugated diene-type flexible copolymers

Aromatic vinyl hydrocarbon/conjugated diene random copolymers or block copolymers or hydrogenation products of these copolymers are used as the aromatic vinyl hydrogen/conjugated diene flexible copolymers used as the flexible polymers.

Specific examples incluide styrene/butadiene block copolymer rubber, styrene/butadiene/styrene block copolymer rubber, styrene/isoprene block copolymer rubber, styrene/isoprene/styrene block copolymer rubber, hydrogenated styrene/butadiene/styrene block copolymer rubber, hydrogenated styrene/isoprene/styrene block copolymer rubber, and styrene/butadiene random copolymer rubber.

In these copolymer rubbers, the mole ratio of the recurring units derived from the aromatic vinyl hydrocarbon to the recurring units derived from the conjugated diene is usually from 10:90 to 70:30. The hydrogenated copolymer rubbers are copolymer rubbers obtained by hydrogenating the double bonds remaining in the copolymer rubbers partly or wholly.

(5) Flexible polymers or copolymers comprising isobutylene or isobutylene and a conjugated diene

Specific examples of the flexible polymer or copolymer (5) are polyisobutylene rubber, polyisoprene rubber, polybutadiene rubber and isobutylene/isoprene copolymer rubber.

The flexible copolymers (2) to (5) have nearly the same properties as the cyclo-olefin polymers (1). Usually they have an intrinsic viscosity, measured in decalin at 135 °C, of 0.01 to 10 dl/g, preferably 0.08 to 7 dl/g, a glass transition temperature (Tg) of not more than 0 °C, preferably not more than -10 °C, especially preferably not more than -20 °C, and a crystallinity, measured by X-ray diffractometry, of usually 0 to 10 %, preferably 0 to 7 %, and especially preferably 0 to 5 %.

These flexible polymers (1) to (5) are used after a crosslinked structure is formed in them. They may be blended with the cyclo-olefin polymer (1). Alternatively, after they are blended with the cyclo-olefin polymer (1), a crosslinked structure may be formed. The cyclo-olefin polymer is generally present in an amount of 5 to 150 parts by weight, preferably 5 to 100 parts by weight, especially preferably 10 to 80 parts by weight, as the total amount of the flexible polymers (1) to (5), per 100 parts by weight of the cyclo-olefin addition polymer. By meeting these blending ratio requirement, polymer alloys having impact strength, rigidity, heat distortion temperature, and hardness in a well-balanced combination can be obtained.

Preferably, the polymer alloys have a melt flow index (MFR under the conditions of ASTM-D1238) of 0.1 to 100.

To form a crosslinked structure as above, organic peroxides are usually used. Examples of organic peroxides used to perform crosslinking polymerization include (a) ketone peroxides such as methyl ethyl ketone peroxide and cyclohexanone peroxide; (b) peroxy ketals such as 1,1-bis(t-butylperoxy)cyclohexane)cyclohexane and 2,2-bis-(t-butylperoxy)octane; (c) hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroxyperoxide and 1,1,3,3-tetramethylbutyl hydroperoxide; (d) dialkyl peroxides such as di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; (e) diacyl peroxides such as lauroyl peroxide and benzoyl peroxide; and (f) peroxy esters such as t-butyl peroxyacetate, t-butyl peroxybenzoate and 2,5-dimethyl-2,5-di(benzoyl-peroxy)hexane.

The amount of the organic peroxide component to be incorporated is usually 0.01 to 1 part by weight, preferably 0.05 to 0.5 part by weight, per 100 parts by weight of the cyclo-olefin addition polymer and the flexible polymer combined.

By further including a compound having two or more radical polymerizable functional groups in the molecule at the time of treatment with the organic peroxide, polymer alloys having excellent impact strength can be obtained. Specifically, by carrying out the crosslinking reaction in the presence of the compound having two or more radical polymerizable functional groups in the molecule, the crosslinking efficiency increases.

Examples of the compound having at least two radical-polymerizable functional groups in the molecule include divinylbenzene, vinyl acrylate and vinyl methacrylate. These compounds may be used in an amount of usually not more than 1 part by weight, preferably 0.1 to 0.5 part by weight, per 100 parts by weight of the cyclo-olefin resin and the flexible polymer combined.

By incorporating the above-described flexible polymers, the flexibility of the sheet or film can be improved.

Various additives may be incorporated into the above cyclo-olefin ring-opened (co)polymers, the hydrogenation products of the (co)polymers, the cycloolefin/ethylene addition polymers, and the mixtures of the polymers and the other polymers described above to form the film and sheet of the invention.

Additives

Examples of the additives include heat stabilizers, weatherability stabilizers, antistatic agents, slip agents, antiblocking agents, antihaze agents, lublicants, dyes, pigments, natural oils, synthetic oils, waxes and organic or inorganic fillers.

Examples of stabilizers include phenolic antioxidants such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, alkyl beta-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2,2'-oxamide-bis[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; aliphatic metal salts such as zinc stearate, calcium stearate and calcium 1,2-hydroxystearate; and polyhydric alcohol aliphatic acid esters such as glycerin monostearate, glycerin distearate, pentaerythritol monostearate, pentaerythritol distearate and pentaerythritol tristerate. They may be used either singly or in combination. A combination of tetrakis-(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)pro-pionate]methane, zinc stearate and glycerin monostearate may be cited as an example.

Examples of the organic or inorganic fillers include silica, diatomaceous earth, alumina, titanium dioxide, magnesium oxide, pumice powder, pumice balloons, aluminium hydroxide, magnesium hydroxide, basic magnesium carbonate, dolomite, calcium sulfate, potassium titanate, barium sulfate, mica, asbestos, glass fibers, glass flakes, glass beads, calcium silicate, montmorilonite, bentonite, graphite, aluminium powder, molybdenum sulfide, boron fibers, silicon carbide fibers, polyethylene fibers, polypropylene fibers, polyester fibers and polyamide fibers.

The cyclo-olefin resin and the other components may be mixed by known methods. For example, all of the components may be simultaneously mixed.

The film or sheet of this invention will further be described below.

Production of the sheet or film

The cyclo-olefin polymer blend with the other polymer may be shaped into the form of a film or a sheet by known methods such as a T-die method or an inflation method. The thickness of the sheet or film of this invention may be properly determined by considering its application. The sheet or film of the invention may be unstretched, or monoaxially or biaxially stretched.

The unstretched sheet or film may be prepared as an unstretched press sheet or film.

A monoaxially or biaxially stretched film or sheet may be prepared by stretching an unstretched sheet or film at a temperature above the glass transition temperature. The stretch ratio may be determined properly by considering the desired properties such as strength. The method of stretching may be any of generally used methods such as a roll stretching method, a tenter stretching method or an inflation method.

The method of producing the sheet or film of this invention wil now be described more specifically. The cyclo-olefin polymer blend prepared as above is shaped, for example, by the T-die method or the inflation method to form a sheet or film having a thickness of 0.05 to 5 mm. The resulting unstretched sheet or film may be used as such or after it is

stretched. In the latter case, the unstretched film or sheet is heated to a temperature higher than the glass transition temperature of the polyblend forming the sheet or film, preferably 0 to 60 °C, especially preferably 10 to 40 °C higher than the glass transition temperature. Then, the heated sheet or film is stretched consecutively in the longitudinal direction and the transverse direction, or simultaneously in both directions, for example, at a stretch ratio of 2 to 50 preferably 3 to 30, to give a biaxially stretched film or sheet.

The sheet or film of this invention so obtained has especially superior gas-barrier propery, elongation resistance and ease of tearing. The sheet or film of this invention has good transparency and surface properties. The film or sheet of this invention further has good heat-sealability.

The sheet or film of this invention also has excellent chemical resistance. When, for example, it is immersed for about 24 hours in sulfuric acid, aqueous ammonia, acetone and ethyl acetate, discoloration cracking, deformation, or dissolution do not appreciably occur.

The sheet or film of this invention has excellent properties and is suitable for use as a packaging material, particularly for foods.

Since the sheet or film of this invention is composed of, for example, the cyclo-olefin polymers (1-a), (1-b) and (2), it has excellent gas-barrier property and elongation resistance. When it are used as a container, a packaging material, or as a shielding material, it can permit sufficient storage of an article to be packed.

Furthermore, the sheet or film of this invention can be easily torn. Therefore, a packing material or a tape produced from the sheet or film of the invention can be easily opened or broken by hand.

The following Examples further illustrate the present invention.

The various properties of the sheet or film of the invention can be measured and evaluated by the following methods:

(1) Melt flow index (MFR)

Measured in accordance with ASTM-D1238 at a predetermined temperature (T°C) under a load of 2.16 kg.

(2) Softening temperature (TMA)

A Thermomechanical Analyzer made by E. I. du Pont de Nemours & Co. was used, and by the heat distortion behavior of a sheet having a thickness of 1 mm, the softening temperature was measured. A quartz needle was placed on the sheet, and a load of 49 g was applied. The sheet was heated at a rate of 5 °C/min., and the temperature at which the needle penetrated to sheet to a depth of 0.635 mm was measured, and defined as TMA.

(3) Glass transition temperature

Measured by DSC-20 made by SEIKO Electronics Industry Co., Ltd.Tg was measured at a temperature elevating rate of 10 °C/min.

(4) Haze

Measured in accordance with ASTM-D1003.

(5) Gloss

Measured in accordance with ASTM-D523. The angle of incidence was 60°.

(6) Tensile test

From the product obtained in a working example, a Dumbell-shaped test piece was prepared in accordance with ASTM type IV. Using this test piece, the tensile test was conducted at 23 °C by the method of ASTM-D638.

(7) Film impact

A test piece having a size of 100 x 100 mm was cut out from the shaped article. The impact strength was measured by a film impact tester made by Toyo Seiki. The impact head: diameter 1 inch (2.54 cm).

(8) Tear strength

Measured by the Elmendorf method in accordance with JIS Z1702 at 23 °C.

(9) Heat-sealability

Two test pieces having a size of 120 x 120 mm, taken from the shaped article obtained in a working example were superimposed and heat-sealed by a heat sealer kept at a predetermined temperature under a pressure of 2 kg/cm^2 for 1 second. The heat-sealed test sample was cut in a rectangular shape with a width of 15 cm, and at 23 °C, its strength was measured at angle of 180°. The testing speed was 300 mm/min.

(10) Gas permeability

Oxygen gas permeability

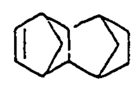
Measured by an oxygen gas permeability tester (OX-TRAN 100, made by Modem Control Co., Ltd.).

Carbon dioxide gas permeability

Measured by using a carbon dioxide gas permeability tester (Mocon Permatranc-IV type, made by Modern Control Co., Ltd).

Comparative Example 1

Pellets (3.4 kg) of a random copolymer of ethylene and 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (structure



to be referred to (ethylene content measured by ^{13}C-NMR: 62 mole %; MFR measured at 220 °C: 35 g/10 min.; intrinsic viscosity measured in decalin at 135 °C: 0.47 dl/g; TMA: 148 °C; Tg: 137 °C) as a cyclo-olefin copolymer were mixed with 0.6 kg of pellets of ethylene/propylene random copolymer (ethylene content: 80 mole %; Tg: -54 °C) as a rubber component. The mixture was melt kneaded by a twin-screw extruder (PCM 45 made by Ikegai Tekko Co., Ltd.) as cylinder temperature of 220 °C and pelletized to form pellets.

A sheet having a thickness of 50 micrometers was prepared from the resulting pellets by a type T-die shaping method by using an extruder having a cylinder diameter of 30 mm. The properties of the sheet were measured.

The results are shown in Table 1.

Example 1

One kilogram of the pellets obtained in Comparative Example 1 were mixed fully with 1 g of Perhexyte 25 Be (Nippon Oils and Fats Co., Ltd.) and 3 g of divinylbenzene. The mixture was reacted in the molten state by a twin-screw extruder (cylinder temperature: 230 °C), and pelletized.

The resulting pellets were formed into a sheet having a thickness of 50 micrometers by the same method as in Comparative Example 1, and its properties were measured. The results are shown in Table 1.

Table 1

Properties	Comparative Example 1	Example 1
Haze (%)	85	-
Gloss (%)	0.5	-
Tensile strength (machine/transverse)		
Stress at yield (kg/cm^2)	430/350	500/640
Stress at break (kg/cm^2)	-	-
Elongation at break (%)	7/20	24/27
Modulus (kg/cm^2)	22/22	-/-

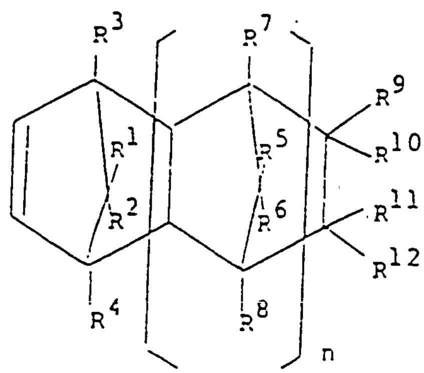
Table 1 (continued)

Properties		Comparative Example 1	Example 1
Film at impact (kg·cm/cm)	at 23°C	1300	1300
	at 0°C	900	1000
Tear strength (machine/transverse) (kg/cm)		1.6/1.8	1.8/2.0
Heat sealability (g/15 mm width)	180°C	-	-
	200°C	570	600
	220°C	1170	1230
Gas permability (cm^3·mm/m^2 24 hrs.atm)	CO_2	-	-
	O_2	-	-

Claims

1. A sheet or a film formed of an intimate mixture of:

(A) at least one cyclo-olefin polymer selected from ring-opened polymers derived from at least one cyclo-olefin of formula (I)



(I)

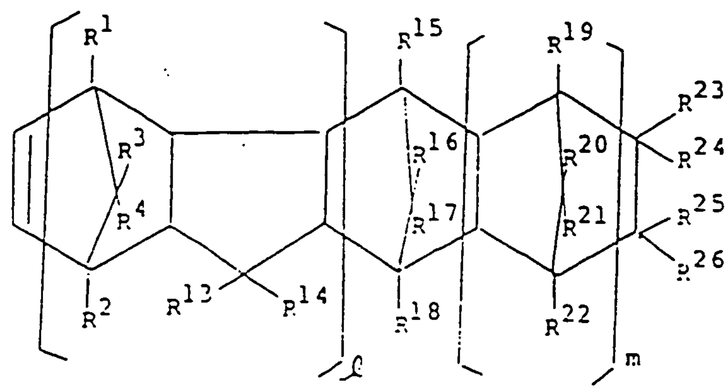
wherein n is 0 or a positive integer, and each of R^1 to R^{12} independently represents hydrogen, a halogen or an aliphatic, aromatic or alicyclic hydrocarbon group; or two of R^9 to R^{12} form, together with the carbon atoms to which they are bonded, a monocyclic or polycyclic group which may contain a double bond; or R^9 and R^{10}, or R^{11} and R^{12} form an alkylidene group together with the carbon atoms to which they are bonded;

ring-opened copolymers derived from the cyclo-olefins of formula (I), hydrogenation products of said polymers or copolymers and addition polymers of the cyclo-olefins of formula (I) with ethylene, said cyclo-olefin polymer having an intrinsic viscosity [η], measured in decalin at 135°C, of 0.01 to 10 dl/g and a softening temperature of at least 70°C; and

(B) at least one crosslinked polymer selected from (1) a flexible copolymer comprising ethylene, another alpha-olefin, and a cyclo-olefin of formula (I), which cyclo-olefin may be the same or different from the cycloolefin used in component (A) and which has an intrinsic viscosity, measured in decalin at 135°C, of 0.01 to 10 dl/g, and a glass transition temperature of not more than 0°C, (2) amorphous or low-crystalline alpha-olefin copolymers formed from at least two alpha-olefins and having a glass transition temperature of not more than 0°C, (3) alpha-olefin/diene copolymers formed from at least two alpha-olefins and at least one conjugated diene and having a glass transition temperature of not more than 0°C, (4) aromatic vinyl hydrocarbon/conjugated diene random or block copolymers or hydrogenation products thereof having a glass transition temperature of not more than 0°C, and (5) flexible polymers formed from isobutylene and flexible copolymers formed from isobutylene and conjugated dienes.

2. A sheet or film according to claim 1 wherein, in formula (I), each of R^1 to R^{12} independently represents a linear or branched C_1-C_{20} alkyl group, a cyclohexyl group or an optionally substituted phenyl groups; or either R^9 or R^{10}, together with either R^{11} or R^{12} form, with the carbon atoms to which they are attached, a monocyclic or polycyclic hydrocarbon group, optionally substituted by a C_1-C_6 alkyl group and containing from 5 to 20 carbon atoms in the cyclic system.

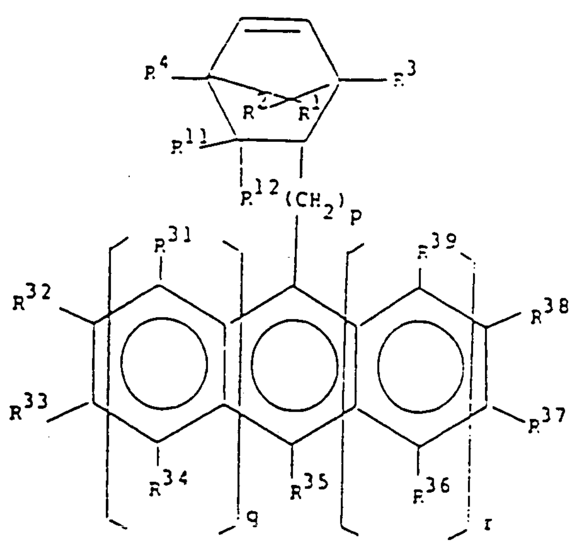
3. A sheet or film according to claim 1 in which the cyclo-olefin polymer is derived from a cyclo-olefin of formula (II)



(II)

wherein R^1 to R^4 are as defined in claim 1 for formula (I), each of R^{13} to R^{26} independently represents hydrogen, a halogen or an aliphatic, aromatic or alicyclic hydrocarbon group; or two of R^{23} to R^{26} form, together with the carbon atoms to which they are bonded, a monocyclic or polycyclic group which may have a double bond; or R^{23} and R^{24}, or R^{25} and R^{26} form, together with the carbon atoms to which they are bonded, an alkylidene group; and 1 is 0 or 1, and m is 0 or a positive integer.

4. A sheet or film according to claim 1 in which the cyclo-olefin polymer is derived from a cyclo-olefin of the following formula (II-a)



(II-a)

wherein p is 0 or an integer of at least 1, and q and r are 0, 1 or 2; R^1 to R^4, R^{11} and R^{12} are as defined in claim 1, 2 or 3; each of R^{31} to R^{39} independently represents hydrogen, a halogen, an alkoxy group, an aliphatic hydrocarbon group or an aromatic hydrocarbon group; and wherein any one of R^{11}, R^{12}, R^{31} and R^{32} is bonded to the adjacent carbon atom either directly or via an alkylene group having 1 to 3 carbon atoms.

5. A sheet or a film according to any one of claims 1 to 4 in which the cyclo-olefin of formula (I), (II) or (II-a) is selected

from

bicyclo[2.2.1]hept-2-ene derivatives,
tetracyclo[4,4,0,$1^{2.5}$,$1^{7.10}$]-3-dodecene derivatives,
hexacyclo[6,6,1,$1^{3.6}$,$1^{10.13}$,$0^{2.7}$,$0^{9.14}$]-4-heptadecene derivatives,
octacyclo[8,8,0,$1^{2.9}$,$1^{4.7}$,$1^{11.18}$,$1^{13.16}$,$0^{3.8}$, $0^{12.17}$]-5-docosene derivatives,
pentacyclo[6,6,1,$1^{3.6}$,$0^{2.7}$,$0^{9.14}$]-4-hexadecene derivatives,
heptacyclo-5-eicosene derivatives,
heptacyclo-5-heneicosene derivatives,
tricyclo[4,3,0,$1^{2.5}$]-3-decene derivatives,
tricyclo[4,3,0,$1^{2.5}$]-3-undecene derivatives,
pentacyclo[6,5,1,$1^{3.6}$,$0^{2.7}$,$0^{9.13}$]-4-penta-decene derivatives,
pentacyclopentadecadiene derivatives,
pentacyclo[4,7,0,$1^{2.5}$,$0^{8.13}$,$1^{9.12}$]-3-penta-decene derivatives,
heptacyclo[7,8,0,$1^{3.6}$,$0^{2.7}$,$1^{10.17}$,$0^{11.16}$,$1^{12.15}$]-4-eicosene derivatives, and
nonacyclo[9,10,1,$1^{4.7}$,$0^{3.8}$,$0^{2.10}$,$0^{12.21}$,$1^{13.20}$, $0^{14.19}$,$1^{15.18}$]-5-pentacosene derivatives.

6. A film or sheet according to any one of the preceding claims which is unstretched, or monoaxially or biaxially stretched.

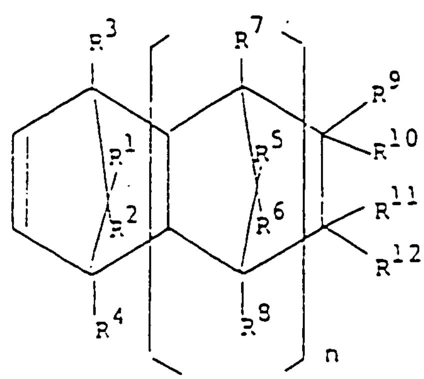
7. A method of preparing a sheet or film which comprises forming a polymer mixture as defined in any one of claims 1 to 5 into a sheet or film.

8. A method according to claim 7 which includes the additional steps of heating the sheet or film to a temperature above the glass transition temperature of the polymer and stretching the heated sheet or film.

Patentansprüche

1. Folie oder Film aus einem innigen Gemisch aus

(A) mindestens einem Cycloolefin-Polymer, ausgewählt aus ring-geöffneten Polymeren, abgeleitet von mindestens einem Cycloolefin der Formel (I)



(I)

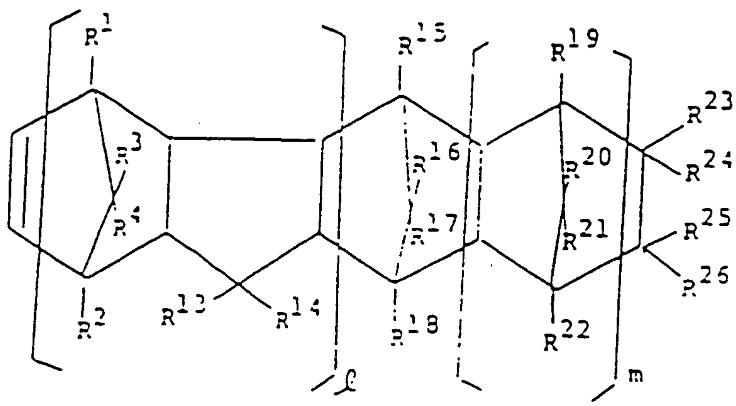
in der n 0 oder eine positive ganze Zahl ist und jedes R^1 bis R^{12} unabhängig Wasserstoff, Halogen oder eine aliphatische, aromatische oder alicyclische Kohlenwasserstoffgruppe bedeutet oder zwei der Reste R^9 bis R^{12} zusammen mit den Kohlenstoffatomen, an die sie gebunden sind, eine monocyclische oder polycyclische Gruppe bilden, die eine Doppelbindung enthalten kann, oder R^9 und R^{10} oder R^{11} und R^{12} zusammen mit den Kohlenstoffatomen, an die sie gebunden sind, eine Alkylidengruppe bilden;

ring-geöffneten Copolymeren, die abgeleitet sind von den Cycloolefinen der Formel (I), hydrierten Produkten der Polymere oder Copolymere und Additionspolymere der Cycloolefine der Formel (I) mit Ethylen, wobei das Cycloolefinpolymer eine Grundviskosität [η], gemessen in Decalin bei 135°C, von 0,01 bis 10 dl/g und eine Erweichungstemperatur von mindestens 70°C besitzt und

(B) mindestens einem vernetzten Polymer, ausgewählt aus (1) einem flexiblen Copolymer, umfassend Ethylen, ein anderes α-Olefin und ein Cycloolefin der Formel (I), wobei das Cycloolefin das gleiche oder ein anderes sein kann wie/als das in der Komponente (A) verwendete Cycloolefin und eine Grundviskosität, gemessen in Decalin bei 135°C, von 0,01 bis 10 dl/g und eine Glasübergangstemperatur von nicht mehr als 0°C besitzt, (2) amorphen oder gering kristallinen α-Olefin-Copolymeren, gebildet aus mindestens zwei α-Olefinen und mit einer Glasübergangstemperatur von nicht mehr als 0°C, (3) α-Olefin/Dien-Copolymeren, gebildet aus mindestens zwei α-Olefinen und mindestens einem konjugierten Dien mit einer Glasübergangstemperatur von nicht mehr als 0°C, (4) statistischen oder Block-Copolymeren von aromatischem Vinylkohlen-wasserstoff/konjugiertem Dien oder hydrierten Produkten davon mit einer Glasübergangstemperatur von nicht mehr als 0°C und (5) flexiblen Polymeren, gebildet aus Isobutylen und flexiblen Copolymeren, gebildet aus Isobutylen und konjugierten Dienen.

2. Folie oder Film nach Anspruch 1, wobei in Formel (I) jedes R^1 bis R^{12} unabhängig eine lineare oder verzweigte C_1-C_{20}-Alkyl-gruppe, eine Hexylgruppe oder eine gegebenenfalls substituierte Phenylgruppe bedeutet oder entweder R^9 oder R^{10} zusammen mit entweder R^{11} oder R^{12} mit den Kohlenstoffatomen, an die sie gebunden sind, eine monocyclische oder polycyclische Kohlenwasserstoffgruppe bilden, gegebenenfalls substituiert durch eine C_1-C_6-Alkylgruppe und enthaltend 5 bis 20 Kohlenstoffatome in dem cyclischen System.

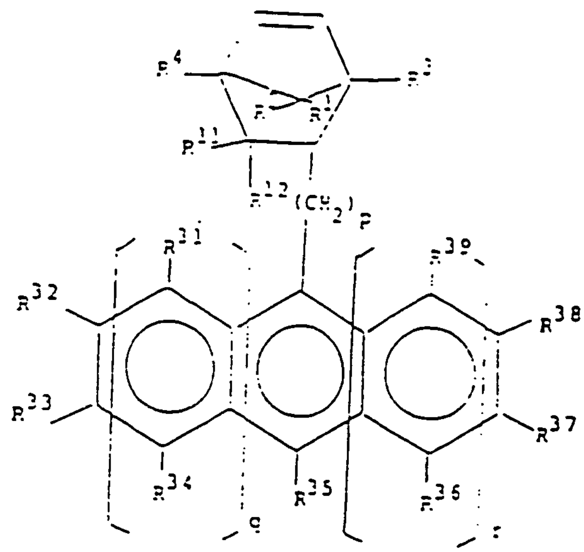
3. Folie oder Film nach Anspruch 1, wobei das cycloolefinpolymer abgeleitet ist von einem Cycloolefin der Formel (II)



(II)

wobei R^1 bis R^4, wie in Anspruch 1, für die Formel (I) definiert sind, jedes R^{13} bis R^{26} unabhängig Wasserstoff, Halogen oder eine aliphatische, aromatische oder alicyclische Kohlenwasserstoffgruppe bedeutet oder zwei der Reste R^{23} bis R^{26} zusammen mit den Kohlenstoffatomen, an die sie gebunden sind, eine monocyclische oder polycyclische Gruppe bilden, die eine Doppelbindung enthalten kann, oder R^{23} und R^{24} oder R^{25} und R^{26} zusammen mit den Kohlenstoffatomen, an die sie gebunden sind, eine Alkylidengruppe bilden und l 0 oder 1 ist und m 0 order eine positive ganze Zahl ist.

4. Folie oder Film nach Anspruch 1, wobei das Cycloolefinpolymer abgeleitet ist von einem Cycloolefin der folgenden Formel (II-a)



(II-a)

wobei p 0 oder eine ganze Zahl von mindestens 1 ist und q und r 0, 1 oder 2 sind, R^1 bis R^4, R^{11} und R^{12}, wie in Anspruch 1, 2 oder 3 definiert sind, jedes R^{31} und R^{39} unabhängig Wasserstoff, Halogen, eine Alkoxygruppe, eine aliphatische Kohlenwasserstoffgruppe oder eine aromatische Kohlenwasserstoffgruppe bedeutet und wobei irgendeiner der Reste R^{11}, R^{12}, R^{31} und R^{32} an das benachbarte Kohlenstoffatom entweder direkt oder über eine Alkylengruppe mit 1 bis 3 Kohlenstoffatomen gebunden ist.

5. Folie oder Film nach einem der Ansprüche 1 bis 4, wobei das Cycloolefin der Formel (I), (II) oder (II-a) ausgewählt ist aus

Bicyclo[2.2.1]hept-2-en-Derivaten,
Tetracyclo[4.4.0.$1^{2.5}1^{7.10}$]-3-dodecen-Derivaten,
Hexacyclo[6.6.1.$1^{3.6}$.$1^{10.13}$.$0^{2.7}$.$0^{9.14}$]-4-heptadecen-Derivaten,
Octycyclo[8.8.0.$1^{2.9}$.$1^{4.7}$.$1^{11.18}$.$1^{13.16}$.$0^{3.8}$.$0^{12.17}$]-5-docosen-Derivaten,
Pentacyclo[6.6.1.$1^{3.6}$.$0^{2.7}$.$0^{9.14}$]-4-hexadecen-Derivaten,
Heptacyclo-5-eicosen-Derivaten,
Heptacyclo-5-heneicosen-Derivaten,
Tricyclo[4.3.0.$1^{2.5}$]-3-decen-Derivaten,
Tricyclo[4.3.0.$1^{2.5}$]-3-undecen-Derivaten,
Pentacyclo[6.5.1.$1^{3.6}$.$0^{2.7}$.$0^{9.13}$]4-penta-decen-Derivaten,
Pentacyclopentadecadien-Derivaten,
Pentacyclo[4.7.0.$1^{2.5}$.$0^{8.13}$.$1^{9.12}$]-3-penta-decen-Derivaten,
Heptacyclo[7.8.0.$1^{3.6}$.$0^{2.7}$.$1^{10.17}$.$0^{11.16}$.$1^{12.15}$]-4-eicosen-Derivaten, und
Nonacyclo[9.10.1.$1^{4.7}$.$0^{3.8}$.$0^{2.10}$.$0^{12.21}$.$1^{13.20}$.$0^{14.19}$.$1^{15.18}$]-5-pentacosen-Derivaten.

6. Film oder Folie nach einem der vorangehenden Ansprüche, die nicht gestreckt oder monoaxial oder biaxial getreckt ist.

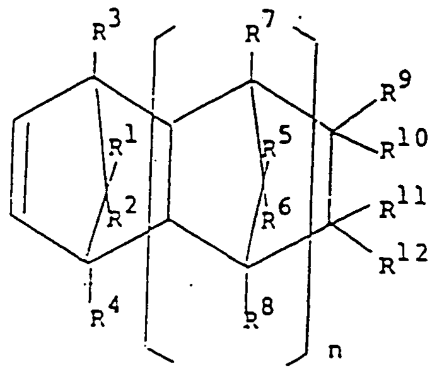
7. Verfahren zur Herstellung einer Folie oder eines Films, umfassend das Formen eines Polymergemisches nach einem der Ansprüche 1 bis 5 zu einer Folie oder einem Film.

8. Verfahren nach Anspruch 7, umfassend die zusätzliche Stufe des Erhitzens der Folie oder des Films auf eine Temperatur oberhalb der Glasübergangstemperatur des Polymers und Strecken der erhitzten Folie oder des Films.

Revendications

1. Feuille ou film formé par un mélange intime de :

(A) au moins un polymère de cyclo-oléfine choisi parmi des polymères obtenus par ouverture de cycles et dérivés d'au moins une cyclo-oléfine de formule (I) :



(I)

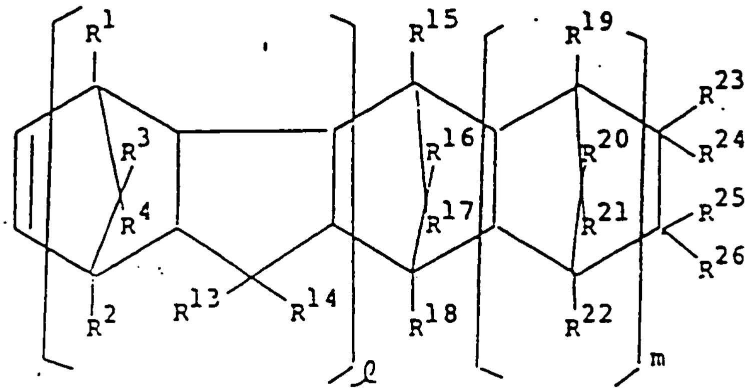
dans laquelle n vaut 0 ou un nombre entier positif, et chacun des symboles R^1 à R^{12} représente indépendamment un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné alicyclique, aromatique ou aliphatique ; ou deux des symboles R^9 à R^{12} forment ensemble, avec les atomes de carbone auxquels ils sont reliés, un groupe monocyclique ou polycyclique qui peut contenir une double liaison ; ou R^9 et R^{10}, ou R^{11} et R^{12} forment ensemble un groupe alkylidène avec les atomes de carbone auxquels ils sont reliés ;

des copolymères obtenus par ouverture de cycles et dérivés de cyclo-oléfines de formule (I), des produits d'hydrogénation desdits polymères ou copolymères et des polymères d'addition de cyclo-oléfines de formule (I) avec l'éthylène, ledit polymère de cyclo-oléfine présentant une viscosité intrinsèque [η], mesurée dans la décaline à 135° C, valant de 0,01 à 10 dl/g et une température d'amollissement d'au moins 70° C ; et

(B) au moins un polymère réticulé choisi parmi (1) un copolymère souple comprenant l'éthylène, une autre α-oléfine, et une cyclo-oléfine de formule (I), laquelle cyclo-oléfine peut être identique ou différente de la cyclo-oléfine utilisée dans le composant (A) et qui a une viscosité intrinsèque, mesurée dans la décaline à 135° C, valant de 0,01 à 10 dl/g, et une température de transition vitreuse d'au plus 0° C, (2) des copolymères d'alpha-oléfine amorphes ou faiblement cristallins formés à partir d'au moins deux alpha-oléfines et présentant une température de transition vitreuse d'au plus 0° C, (3) des copolymères alpha-oléfine/diène formés à partir d'au moins deux alpha-oléfines et d'au moins un diène conjugué et présentant une température de transition vitreuse d'au plus 0° C, (4) des copolymères séquencés ou statistiques hydrocarbure vinylique aromatique/diène conjugué ou leurs produits d'hydrogénation présentant une température de transition vitreuse d'au plus 0° C, et (5) des polymères souples formés à partir d'isobutylène et des copolymères souples formés à partir d'isobutylène et de diènes conjugués.

2. Feuille ou film conforme à la revendication 1, dans lequel dans la formule (I), chacun des symboles R^1 à R^{12} représente indépendamment un groupe alkyle linéaire ou ramifié en C_1-C_{20}, un groupe cyclohexyle, ou un groupe phényle éventuellement substitué ; ou R^9 ou R^{10}, avec R^{11} ou R^{12} forment ensemble, avec les atomes de carbone auxquels ils sont reliés, un groupe hydrocarboné polycyclique ou monocyclique, éventuellement substitué par un groupe alkyle en C_1-C_6 et comportant de 5 à 20 atomes de carbone dans la structure cyclique.

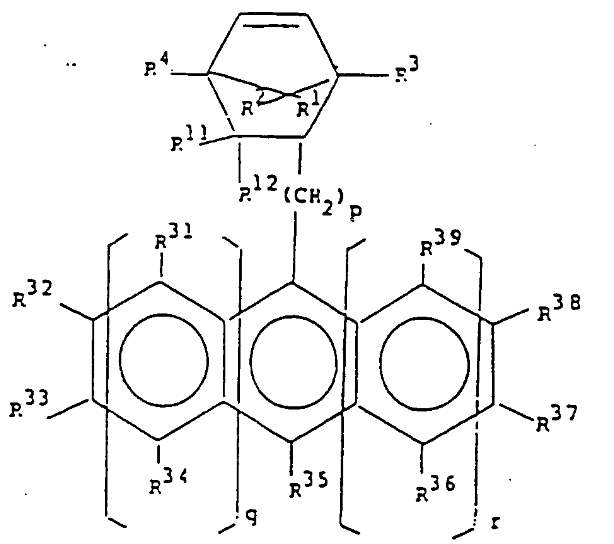
3. Feuille ou film conforme à la revendication 1, dans lequel le polymère de cyclo-oléfine est dérivé d'une cyclo-oléfine de formule (II) :



(II)

dans laquelle les symboles R^1 à R^4 sont tels que définis dans la revendication 1 pour la formule (I), chacun des symboles R^{13} à R^{26} représente indépendamment un atome d'hydrogène, un atome d'halogène, un groupe hydrocarboné alicyclique, aromatique ou aliphatique ; ou deux des symboles R^{23} à R^{26} forment ensemble, avec les atomes de carbone auxquels ils sont reliés, un groupe monocyclique ou polycyclique qui peut avoir une double liaison ; ou R^{23} et R^{24} ou R^{25} et R^{26} forment ensemble, avec les atomes de carbone auxquels ils sont reliés, un groupe alkylidène ; et 1 vaut 0 ou 1, et m vaut 0 ou un nombre entier positif.

4. Feuille ou film conforme à la revendication 1, dans lequel le polymère de cyclo-oléfine est dérivé d'une cyclo-oléfine répondant à la formule suivante (II-a) :



(II-a)

dans laquelle p vaut 0 ou un nombre entier valant au moins 1, et q et r valent 0, 1 ou 2 ; les symboles R^1 à R^4, R^{11} et R^{12} sont tels que définis dans la revendication 1, 2 ou 3 ; chacun des symboles R^{31} à R^{39} représente indépendamment un atome d'hydrogène, un atome d'halogène, un groupe alcoxy, un groupe hydrocarboné aliphatique ou un groupe hydrocarboné aromatique ; et dans laquelle l'un quelconque des symboles R^{11}, R^{12}, R^{31} et R^{32} est relié à l'atome de carbone adjacent soit directement, soit par l'intermédiaire d'un groupe alkylène comportant de 1 à 3 atomes de carbone.

5. Feuille ou film conforme à l'une quelconque des revendications 1 à 4, dans lequel la cyclo-oléfine de formule (I), (II) ou (II-a) est choisie parmi les

dérivés de bicyclo[2.2.1]hept-2-ène,
dérivés de tétracyclo[4.4.0.$1^{2.5}$.$1^{7.10}$]-3-dodécène,
dérivés d'hexacyclo[6. 6. 1. $1^{3.6}$.$1^{10.13}$. $0^{2.7}$.$0^{9.14}$]-4-heptadécène,

dérivés d'octacyclo[8, 8, 0, $1^{2.9}$, $1^{4.7}$, $1^{11.18}$, $1^{13.16}$, $0^{3.8}$, $0^{12.17}$]-5-docosène,
dérivés de pentacyclo[6, 6, 1, $1^{3.6}$, $0^{2.7}$, $0^{9.12}$]-4-hexadécène,
dérivés d'heptacyclo-5-eicosène,
dérivés d'heptacyclo-5-heneicosène,
dérivés de tricyclo[4, 3, 0, $1^{2.5}$]-3-décène,
dérivés de tricyclo[4, 3, 0, $1^{2.5}$]-3-undécène,
dérivés de pentacyclopentadécadiène,
dérivés de pentacyclo[6, 5, 1, $1^{3.6}$, $0^{2.7}$, $0^{9.13}$]-4-penta-décène,
dérivés de pentacyclopentadécadiène,
dérivés de pentacyclo[4, 7, 0, $1^{2.5}$, $0^{8.13}$, $1^{9.12}$]-3-penta-décène,
dérivés d'heptacyclo[7, 8, 0, $1^{3.6}$, $0^{2.7}$, $1^{10.17}$, $0^{11.16}$, $1^{12.15}$]-4-eicosène, et
dérivés de nonacyclo[9, 10, 1, $1^{4.7}$, $0^{3.8}$, $0^{2.10}$, $0^{12.21}$, $1^{13.20}$, $0^{14.19}$, $1^{15.18}$] -5-pentacosène.

6. Feuille ou film conforme à l'une quelconque des précédentes revendications qui n'est pas étiré, ou qui est soumis à un étirage monoaxial ou biaxial.

7. Procédé de préparation d'une feuille ou d'un film, qui comprend le fait de transformer un mélange de polymères conforme à l'une quelconque des revendications 1 à 5 en une feuille ou un film.

8. Procédé conforme à la revendication 7 qui englobe les étapes supplémentaires de chauffage d'une feuille ou d'un film à une température supérieure à la température de transition vitreuse du polymère et étirage du film ou de la feuille chauffés.